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NEW CATHODE-ANODE COUPLES FOR SECONDARY BATTERIES

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APRIL 1961

FLIGHT ACCESSORIES LABORATORY

CONTRACT NR. AF 33(616)-7505
PROJECT NR. 3145
TASK NR. 61079

XEROX

62-1-5

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Radio Corporation of America, Somerville, New Jersey, on Air Force contract AF33(616)-7505, under Task Nr 61079 of Project Nr 3145, "Energy Conversion Technology". The work was administered under the direction of the Flight Accessories Laboratory, Wright Air Development Division. Mr. J. E. Cooper was task engineer for the laboratory.

The studies presented began in June 1960, were concluded in December 1960.

ABSTRACT

The prime objective of this program is to provide design criteria for long-life light-weight secondary batteries through the investigations of new cathode-anode couples and their associated electrolytes and separators.

The new cathode-anode couples to be studied will have a theoretical energy-to-weight ratio of reactant materials based on the free-energy release of the reactant materials at 25°C of not less than 500 watt-hours per pound.

A classification of anode and cathode materials based on similar chemical and physical properties was developed to select couples and their associated electrolytes and separators to provide design criteria for long-life light-weight secondary batteries.

The couples offering the most promise utilize an anode selected from the low molecular weight alkali metals, alkaline-earth metals or aluminum and a cathode from the metal oxides with a high oxygen content or a metal-metal ion electrode. A molten salt solvent system was shown to be the most desirable electrolyte for the development of a secondary battery.

The anode materials are the limiting reactant materials in the selection of new anode-cathode couples for long-life, light-weight secondary batteries in that they determine the solvent system to be used as the electrolyte. Lithium, sodium, magnesium, calcium, and aluminum are the most desirable anode materials on the basis of reactivity and ampere-hour capacity. The available literature

shows a molten salt electrolyte, in contrast to other solvent systems, to be the most desirable because:

    a. These anodes are reversible in certain molten salts.

    b. Electrodes may be designed which do not polarize appreciably.

    c. Molten salts have a high electrical conductivity.

A ceramic or porcelain membrane, in which sodium or similar ions are mobile, can best meet the requirements of a separator in molten salt electrolyte. Experimental data show that these materials can prevent the mixing of the above reactant materials. A porous separator can be used when the reactant materials have a low solubility in the molten salt electrolyte.

The best cathode materials on the basis of capacity, reversibility and stability in molten salts are:

    a. Metal oxides

    b. Metal-metal ion electrodes

Some of the recommended couples for experimental evaluation are:

    a. Na/NaCl/Cer/AgCl/Ag

    b. Na/NaCl,LiCl/Cer/Cu_2O/Cu

    c. Li/LiCl,NaCl/Cer/AgCl/Ag

    d. Li/LiCl,NaCl/Cer/CuCl/Cu

    e. Mg/$MgCl_2$,NaCl/Cer/AgCl/Ag

    f. Mg/$MgCl_2$,NaCl/Cer/CuCl/Cu

    g. Na/NaCl/Cer/PdO/Pd

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PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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1. PURPOSE

The prime objective of this program is to provide design criteria for long-life light-weight secondary batteries through the investigations of new cathode-anode couples and their associated electrolytes and separators.

The new cathode-anode couples to be studied will have a theoretical energy-to-weight ratio of reactant materials based on the free-energy release of the reactant materials at 25°C of not less than 500 watt-hours per pound.

2. INTRODUCTION

2.1 Objectives of Program

The prime objective of this contract is to provide design criteria for the development of long-life, light-weight secondary batteries through the investigation of new anode-cathode couples and their associated electrolytes and separators.

The new anode-cathode materials to be studied in this program are those which have a theoretical energy to weight ratio of reactant materials based on the free energy release of the reactant materials at $25^\circ C$ of not less than 500 watt-hours per pound.

The requirements and design goals of this program outlined in technical requirements PR92034 are:

a. The battery system shall be stable on open circuit (not subject to self-discharge).

b. The battery system shall have a high free energy content (the chemical energy being readily convertible to electrical energy and vice versa).

c. The battery shall be completely self contained without the addition of any energy other than electricity.

d. The battery shall be capable of operation in any temperature ranging from $0^\circ F$ to $120^\circ F$.

e. The battery should be capable of operation in a space environment.

f. The battery shall be capable of operation in any position.

g. Maximum life under repeated discharge-charge cycles at rated capacity shall be a prime consideration.

h. Minimum volume shall be considered.

During the program, the following are to be considered but shall in no way limit the study:

a. Unique methods of construction such as lamination of the plates and separators with solid electrolytes.

b. Hermetic sealing of the battery for space application.

c. Methods of construction which would obviate hermetic sealing of the battery for space application.

d. Ion exchange membranes for use as separators.

This program will not preclude the investigation of either the noble metals or rare earths because of their apparent cost or scarcity.

2.1.1 Outline of Report

This report develops a classification of the reactant materials into groups with similar chemical and physical properties. In the selection of these materials, there were no restrictions placed on the reactant materials as to feasibility of their use in a secondary battery. A general discussion of the possible anode and cathode materials is then presented with a preliminary selection of the classes of anodes and cathode materials which best meet the requirements of the study. In this selection, it is shown that the anode materials are the limiting reactive component with respect to electrolyte type and that the alkali and alkaline-earth metals and aluminum are the most desirable materials. In view of this restriction, a detailed discussion of electrolyte types, organic media, liquid ammonia,

molten salts, etc., with respect to the feasibility of developing an electrode with these materials is presented. A detailed discussion of molten salts, the most promising class of electrolytes, is given along with recommendations for couples for experimental evaluation.

2.2 Discussion of Available Materials

2.2.1 Introduction and Classification of Possible Reactant Materials

The most direct and systematic approach to the selection of the most promising materials is through a consideration of the ampere-hour per pound capacity and half-cell potential of some possible anode and cathode materials. This method gives the same result as dividing the free energy release of the reactant materials by the molecular weight of the reactant materials because

$$- \Delta F = nFE$$

where $- \Delta F$ is the change in free energy of the cell reaction, n is the number of equivalents of electricity associated with one molar unit of the cell reaction, F is the Faraday and E is the reversible e.m.f.

Data for the pounds of material required to supply 500 ampere-hours of electrical energy and the theoretical reversible potential of some cathode materials are given in Table I and similar data for anode materials are given in Table II. It is recognized that many of the potentials, in particular those in Table II, are values calculated from other thermodynamic data, and are not attainable in aqueous electrolytes. It will be shown later that the ampere-hour capacity is the dominant factor in determining the capacity of various couples.

The theoretical capacity (C) in watt-hours per pound of various couples
can be calculated from the data in Tables I and II by the following
equation:

$$C = 500 \; \frac{E_a - E_c}{lb_a + lb_c} \tag{1}$$

where E_a is the reversible e.m.f. of the anode, E_c is the reversible e.m.f.
of the cathode, lb_a is the weight in pounds of anode material required to
supply 500 ampere-hours electrical energy, and lb_c is the weight in pounds
of cathode material required to supply 500 ampere-hours of electrical energy.

This equation shows that the desirable materials should both have a high
ampere-hour per pound capacity and, that, if one of the reactant materials
does not have a high capacity, $E_a - E_c$ must be large. The ratio within the
brackets must also be greater than 1 for a particular couple to have
theoretical capacity greater than 500 watt-hours per pound.

It is seen by this equation and the data in Tables I and II that the ampere-
hour capacity, $lb_a + lb_c$, is the dominant factor in the selection of avail-
able materials. This is further substantiated by data for the e.m.f. of
some of these anode and cathode materials compared in various solvents as
shown in Table III. It should be noted that the theoretical e.m.f. in the
various electrolyte systems does not vary enough to change general conclu-
sions on the classes of available anode and cathode materials listed above.
This is particularly true of the anode materials later shown to be the
limiting component in the selection of electrolyte systems.

A detailed listing of theoretical capacities was not given because such a listing would require a critical evaluation of the sources of information, such as the free energy of ions and standard states in these solvents, which is beyond the scope of the present study.

Presented in Table IV are the estimated theoretical capacities of various anode-cathode combinations calculated from the above equation. For ease of discussion, the available cathode materials listed in Tables I and III may be grouped into four general classes:

    a. Low-molecular-weight elements, e.g., F_2, Cl_2, O_2, H_2, and S.

    b. Inorganic compounds with a high available oxygen content, e.g., OsO_4, CuO, AgO, NiO_2, and MnO_2 (2 electron change).

    c. Metal-metal ion electrodes

        $Cu^{++} \rightarrow Cu$, $Ag^+ \rightarrow Ag$, $Rh^{++} \rightarrow Rh$, $Sb^{+++} \rightarrow Sb$

    d. Organic materials, e.g., quinone, nitroguanidine.

The available anode materials on the basis of their ampere-hour capacity and theoretical e.m.f. in aqueous electrolytes may be classed as follows:

    a. The low-molecular-weight metals in Group IA, IIA, and Al.

    b. Hydrogen

    c. Metals in the fourth row in Groups VI, VII, and VIII.

    d. Boron and its hydrides.

    e. Carbon and its derivatives.

2.3 General Properties of Anodes, Electrolytes, and Cathodes and Preliminary Selection of Reactant Materials

2.3.1 Introduction

The general physical and chemical properties of the various classes of anode and cathode materials pertinent to the development of secondary

batteries are presented in the following sections. Some of the properties that were considered are:

a. Reversibility - The first requirement of an electrode in a secondary battery under normal operating conditions is that it does not polarize appreciably, i.e., behave nearly reversibly. In reviewing the literature, this was given first consideration. When data were lacking, as is in the case of some non-aqueous electrolytes, the electrode efficiency was used as a clue to the reversibility of the electrode. If the electrode efficiency did not approach 100 per cent, it was assumed that side reactions prevented the electrode from behaving reversibly.

b. Handling Properties - The general problems to be expected in handling the materials and their effects on the final performance of the system were considered. Such factors as the physical state and the chemical reactivity of the materials were considered, and are pointed out when they place restrictions on the final system.

c. Capacity of Reactant Materials and Current Studies - When the capacity of the reactant materials as calculated above was near 500 watt-hours per pound, the desirability of studying these couples was considered with respect to current studies on related systems. This applies mainly to the anode materials in the fourth row of the Periodic Chart in Groups VI, VII and VIII and hydrogen.

The following discussion is oriented toward the anode materials since it will be shown later that these materials place the major restrictions on feasible electrolyte systems. After the anodes and these electrolytes,

the cathode materials are discussed taking into account the restrictions placed on the system by the anode and electrolyte.

2.3.2 Anode Materials

The alkali and alkaline-earth metals and aluminum are the most desirable anode materials on the basis of ampere-hour capacity and theoretical e.m.f. in aqueous systems with respect to the various cathode materials listed. These metals permit a wider choice of cathode materials than do any of the other classes of anode materials. The development of a reversible electrode utilizing these materials is limited by the fact that they are highly irreversible in aqueous electrolytes and other electrolytes with labile hydrogen atoms.

The handling of these materials will require special precautions, such as inert atmospheres, which are discussed in greater detail along with recommendations for specific systems. It should be noted that the handling properties of these materials are well known.

The high capacity anode materials in the fourth row of the periodic chart in Groups VI, VII and VIII must be coupled with cathode materials that have both a high ampere-hour capacity and e.m.f. Such cathode materials are fluorine, oxygen, bromates and chromates. None of these cathode materials are attractive for the present purposes as pointed out in section 2.3. Also, with the exception of iron, the design of a reversible cell with these materials does not appear feasible, especially when it is considered that these materials are codeposited with hydrogen.

Although non-aqueous electrolytes could possibly solve some of these problems, because of the limitations placed on the cathode materials by the theoretical e.m.f. and capacity of the anode materials, these anode materials will not be considered further in this study.

The hydrogen-oxygen couple is the most attractive couple using a hydrogen anode, but because this system is already under investigation as a secondary battery, hydrogen will not be included in further studies.

Boron and carbon need not be considered further because there are no indications that a reversible electrode can be made with either. The same is true for the various derivatives of these elements with few exceptions. The few reversible organic compounds have high molecular weights.

2.3.2.1 Electrolytes for the Alkali and Alkaline-Earth Metals and Aluminum

A review of the general properties of various electrolyte types is presented because of the irreversibility of the alkali and alkaline-earth metals and aluminum in aqueous electrolytes. The electrolyte types that were considered are:

    a. Liquid ammonia

    b. Organic solvents - The various solvents considered for the electro-deposition of these anode materials were evaluated.

    c. Molten salts - The molten salts in which electrode potential and electro-deposition studies have been made were given most attention.

    d. Miscellaneous electrolytes - Other electrolytes such as solid electrolyte AgCl, and liquid sulfur dioxide, were also considered.

The above limitations to organic solvents and molten salts is based on the assumption that these are the most practical electrolyte systems for the present study. This limitation would also aid considerably in reducing the volume of literature to be evaluated.

It was felt, and later shown, that this restriction would not affect the selection of the most desirable electrolyte type. In the evaluation of the various electrolyte types, the following properties were considered:

    a. Electrode reversibility.

    b. Handling properties.

    c. Current studies.

    d. Conductivity.

    e. Typical operating temperature range.

Items a, b, and c were discussed in Section 2.3.1 while d and e are self-explanatory. A comparison of the electrical conductivity and operating temperature range of some of the electrolytes to be considered is found in Figures 1 and 2.

Organic Solvents

A review of the literature on organic-solvent systems has let to several generalizations concerning their use as electrolytes in secondary batteries. Most of the applicable literature on organic solvents pertains to conductivity measurements. The available literature on organic solvents pertinent to the present study deals mainly with attempts to electro-deposit these anode materials. The electro-deposition of these materials from typical organic solvents has been achieved and is recorded in the recent literature[3,4,5]. A general problem with the older literature is the reliability that can be placed on the data.

Some of the more important generalizations which can be made from the literature are:

a. The work done on electro-deposition indicates that the most desirable solvents are those which readily complex with the solute; e.g., $AlCl_3$ in pyridine, LiCl in dimethylacetamide.

b. From this work on electro-deposition, it appears that aluminum and magnesium offer the most hope for an anode in an organic electrolyte.

c. At present, sufficient information is lacking to permit conclusions to be drawn on cathode materials.

d. The dielectric constant of the solvent cannot be used as a criterion for selection of a suitable solvent, for example, ether, which has a dielectric constant of approximately 4.5, is a good solvent for electro-deposition whereas HCN, with a dielectric constant of 110, is not a good electrolytic solvent.

e. The organic electrolytes are poorer conductors than the typical aqueous electrolytes used in batteries. This will create special problems in the design of electrodes for heavy-drain applications.

f. The complete removal of water from the solvent is necessary.

g. There is a general lack of fundamental information on electrode processes in organic solvents.

The major problem with organic solvents is that there are no known reversible electrodes with these anode materials. This has been stated by Fuoss[13] for non-aqueous electrolytic systems in general, with the exception of ammonia, methanol and ethanol. Presumably this

statement as given refers to organic solvents. Jans and co-workers[14] have questioned the reliability of experimental values of electrode potentials in various solvents and have pointed out the need for sound experimental data in non-aqueous media in order that theoretical concepts can be developed. The available data in the literature for the electro-deposition of the metals corroborates this in that none of these metals have been electro-deposited at electrode efficiencies approaching 100 per cent with few exceptions[3,4,5,7,12].

For these reasons, organic solvents, although attractive as electrolytes for the development of electrodes with alkali and alkaline-earth metals and aluminum with respect to their operating-temperature range and relative ease of handling as compared to molten salts, are not being further explored in this study. It is required that a fundamental study on electrode reactions in organic solvents be made before a program utilizing these materials is considered.

Molten_Salts_

Some of the important generalizations which can be made about molten salts are:

   a. Experimental data show that various anode and cathode materials behave reversibly in certain molten salts[37,57,62].

Some reversible systems that have been reported in the literature are:

   1. $Mg/MgCl_2/Cl_2$ E = 2.544 @ 718°C   (82)

   2. $Al/3NaF//AlF_3/O_2$ (Pt) E = 2.02 @ 1000°C   (84)

b. Comparison of the electrical conductivity of the various classes of electrolytes presented in Figure 1 shows that molten salts are the best electrolytic conductors. The discharge data obtained on thermal cells indicate that polarization of cells with a molten-salt electrolyte will be low. Both factors are favorable to the design of a secondary battery.

c. The operating temperature range will be over 400°C.

The success of couples in molten salts will be determined by solution of the containment problems and problems associated with the solubility of the reactants in the electrolyte. A major design problem will be the development of an electrochemically and thermally adequate separator.

The molten salts, however, offer the most promise for the development of a secondary battery with the alkali and alkaline-earth metals and aluminum. This is because there are considerable experimental data showing that reversible electrodes with these materials are feasible as compared with other electrolyte systems[57,62,70,99]. The most promising couples in molten salts and an experimental program are described in Sections 2.4.5.

Miscellaneous Electrolyte Systems

Liquid ammonia has several desirable properties as a solvent system in battery applications such as the high electrolytic conductivity at low temperatures of liquid ammonia solutions containing various salts. The anode materials under consideration, however, are soluble in liquid ammonia which makes the design of a secondary battery with these materials impractical. The data on the activated stand of reserve batteries (AVA) using magnesium anodes and a liquid ammonia solvent substantiate this conclusion.

Solid electrolytes, such as the silver and copper halides cannot be used for two reasons: low electrical conductivity and low decomposition potentials. The low decomposition potentials prevent their use with the anode and cathode materials under consideration in this program.

Solvent systems such as liquid sulfur dioxide, liquid hydrogen cyanide, and others discussed in standard works on non-aqueous solvents, were not considered because of obvious handling problems or the lack of available information.

2.3.3 Cathode Materials

The inorganic oxide materials stable at high temperatures and the metal-metal ion electrodes are the most desirable cathode materials for the development of a secondary battery with a molten salt electrolyte.

2.3.3.1 Low-Molecular-Weight Elements - The low molecular-weight gases are only practical in an electrochemical system when the weight of the electrodes, apparatus for handling, and storage containers are small compared to the weight of the active materials. This would only be true in large secondary batteries. Although the low-molecular-weight gases have the highest capacity, the problems associated with the design of porous electrodes and the handling of gases will present definite disadvantages for their utilization as cathode materials in secondary batteries. This is particularly true in space environments; e.g., zero gravity, hermetic sealing, access for maintenance of electrodes. It is seen from the data in Tables I and III that oxygen is the most attractive of the low-molecular-weight gases. It is known that oxygen electrodes can be made to operate

efficiently in aqueous and molten salt electrolytes[66][84]. Fluorine and chlorine to a lesser extent, would present problems in handling and storage. Hydrogen because of its low potential does not meet the 500 watt-hours per pound requirement except with a few anode materials, e.g., Li. For this reason and because hydrogen-oxygen and zinc-oxygen secondary batteries are already under investigation, these materials will not be considered further. The use of the known reversible organic materials is ruled out because of their instability at high temperatures. The same is true of any organic compounds that can be foreseen.

2.3.3.2 Inorganic Oxides - The general stability of the various oxides may be noted from their melting and boiling points and decomposition temperatures presented in Table V. Bromates, iodates, chlorates, osmium tetraoxide, chromates, silver oxide, and mercuric oxide decompose at relatively low temperatures and thus are not suitable. Data for the chlorides of the metal-metal ion electrodes are presented in Table VI because the stability of metal chlorides plays a role in the overall stability of certain systems. It should be noted that many of the remaining materials have been shown to be reversible in molten salts as evidenced by the data in Table VIII presented in Section 2.4.3.

Further details on these materials along with selections based on stability, electrode potentials, theoretical capacity and reversibility are discussed in Section 2.4.

2.4 Molten Salt Secondary Batteries

2.4.1 Introduction

This section presents a detailed discussion of the application of molten
salts to the design of secondary batteries. In summarizing the pertinent
literature, certain basic requirements that are placed on the materials
by this application were considered. The major factors considered are:

a. Reversibility of Electrodes and Separation Techniques - The basic
requirement of a secondary battery is that all components entering
into the cell reaction must be reversible. Included in this is
the polarization of the electrodes and their associated electrolyte
and separator under current flow.

b. Solubility of Reactant Materials in Melt - In contrast to aqueous
systems the reactant materials, in particular, the proposed anode
materials are soluble in the electrolyte. This permits the diffu-
sion of the reactant materials throughout the cell and would pre-
vent the design of reversible electrodes due to the side reactions.
The cell also could not maintain a charge or be recharged many times
without serious loss in capacity. Important leads to the solution
of this can be gained from the methods used for the electrochemical
production of these materials. A discussion with recommendations
for the use of a porcelain separator is presented to solve this
problem.

c. Reactivity of the Reactant Materials and Electrolyte at High Tem-
peratures - A consideration of materials that can be used in
laboratory studies to demonstrate feasibility of a given couple and

also for ultimate end use is presented. This is of importance because of the high reactivity of these materials at high temperatures.

d. Miscellaneous - The impurities and their effect on the electrode reactions of these materials are given. Special problems due to the vapor pressure of the reactant materials and electrolytes, electrical contact and containment are presented.

The data are summarized as follows:

a. Anode materials and Containment - This section presents a brief review of the individual anode materials, with emphasis on the problems discussed above, as derived from the literature pertaining to their commercial production, and the AEC data with respect to their use in nuclear reactors. A brief discussion of containment at high temperatures is presented.

b. Methods of Separation - The basic problem of separation in a molten salt secondary battery is examined and methods of solution are presented. Cathode materials and proposed couples are also listed in this section.

c. Experimental Program - A description of the experimental program to demonstrate the feasibility of the selected couples is presented.

d. Cathode Materials - A summary of experimental e.m.f. data for metallic oxide and metal-metal ion electrodes in molten salts is presented.

e. Recommended couples for experimental evaluation are listed.

2.4.2 Anode Materials

2.4.2.1 General Properties of Anode Materials and Electrolysis in Molten Salt

Some physical properties of the alkali and alkaline-earth metals and aluminum and their chlorides are summarized in Table VI.

The validity of Faraday's Law has been demonstrated rigorously for the electrolysis of molten salts. In practice, high current and energy efficiencies are obtained by preventing the mixing of anodic and cathodic materials and by providing inert atmospheres. The major causes of electrode-material loss are:

    a. Distillation, volatilization, or sublimation which may be controlled by temperature regulation.

    b. Mixing of electrode materials by diffusion, which can be decreased by separators.

    c. Formation of metal fogs, which may be controlled by temperature and the addition of neutral salts, and by reduced current density.

    d. Reaction with the gases above the electrodes.

Electrode reactions in molten salts have been shown to occur at appreciable rates with little polarization at their reversible potential. Experimental measurements have been made by Flengas[57], Laitinen[71,72], Delimarskii[44,45,46,47,48], Piontelli[92,93], and their co-workers.

In the commercial production of the alkali metals, alkaline-earth metals and aluminum, the cells are operated at voltages considerably above their theoretical potential due to the anode effect. The anode effect is

caused by the gases that surround the anode during electrolysis and prevent good contact with the electrolyte. A detailed discussion is given by Mantell[79].

2.4.2.2 Alkali Metals

Sodium is produced commercially in the Downes or Knapsack cells. In its production, one of the principal problems is solubility of sodium in the molten electrolyte.

The solubility of sodium in molten electrolytes (NaCl) is low up to 600°C, but increases to a point where the deposition of sodium is impossible at 700°C. The preferred electrolyte in commercial cells is a 58 to 42 ratio of calcium chloride to sodium chloride.

A brief discussion of the miscibility of liquid metals with salts at high temperature is in order because of its importance to the design of a practical secondary battery.

Bredig, Bronstein, Johnson and Smith[39] have studied the liquid-liquid phase equilibria in binary systems composed of an alkali metal with its halide, and have found complete miscibility of the phases at moderately high temperatures (> 1000°C). This critical temperature is known as the "consolute" temperature. Such binary systems are further characterized by a "monotectic" temperature, some 4 to 7°C below the melting point of the pure salt, at which the liquid binary system, on cooling, forms a solid plus another liquid phase of different composition.

From the data for the sodium-sodium halide systems, summarized in Table VII, it is seen that the practical operation of a reversible

electrochemical cell will seek an optimum temperature range in order to maintain a metal phase.

Observations from commercial practice suggest that selected multi-component systems afford less stringent conditions between the "monotectic" and "consolute" temperatures. For example, the use of mixed salts ($CaCl_2$ + NaCl) permits operation of a sodium cell at some 400°C below the critical range[79]. Sodium, at electrolytic-cell operating temperatures, is extremely corrosive toward the common materials used for cell construction, e.g., steels and refractories. Even at 600°C the high vapor pressure of sodium (B.P. = 877°C) demands special apparatus, reflected in elaborate commercial processes[79]. The cathodes are of acid-proof cast steel (brick-walled), and the anodes are of graphite. A 16-mesh steel wire net serves as the diaphram between the electrodes. The bath temperature is maintained by the heat generated from the polarization effects during electrolysis.

Lithium is commercially produced in a sodium type cell, with the metal (d = 0.49) forming a layer upon the molten electrolyte. The electrolyte consists of a mixture of KCl and LiCl, which may also contain LiBr and is electrolyzed at 420°C.

2.4.2.3 Magnesium

Magnesium is produced in the Dow (Michigan) brine process by the electrolysis of a salt mixture consisting of:

$MgCl_2$	25%
NaCl	60%
$CaCl_2$	15%

This salt mixture may also contain small amounts of KCl, $SrCl_2$ and MgO. The MgO causes a sludge but has a definite function in the purification of the magnesium. The specific gravity of the electrolyte is higher than that of molten magnesium, which permits the separation of the magnesium into the upper layer. For this reason, NaCl is preferred to KCl in the electrolyte.

Impurities such as Al, Cu, Zn, Ni, Si, and Mn in the electrolyte become alloyed with product Mg. Iron, boron, and manganese are liberated on the cathode, or are reduced by the Mg floating on the electrolyte bath. Under certain operating conditions these impurities form shells around globules of Mg which reduce the yield of pure metal. Boron in the electrolyte is especially troublesome and must be held to less than 10 ppm. Boron appears at the cathode during electrolysis in the form of metal borides which keep the small Mg spheres from coalescing. Calcium fluoride, added to the melt to remedy this problem, fails at excessive boron concentration. Sulfates are detrimental in the magnesium cell because they can be reduced to sulfur or sulfur dioxide.

2.4.2.4 Aluminum

Aluminum is produced by electrolysis of Al_2O_3 solutions in AlF_3 with a fluoride of a metal more electropositive than Al (i.e., Na, K, Ca). Aluminum fluoride is used because molten aluminum chloride is a poor conductor. The high reactivity of these molten salts and of molten aluminum is countered by the use of carbon-lined iron containers. The heat from the reaction of anode oxygen with the carbon lining is

utilized to maintain the bath temperature at 960°C. The raw aluminum is further refined to 99.99 per cent purity, using Cu-Al alloy as the heavy bottom layer anode, covered by an electrolyte layer, with an upper-most cathode layer of pure aluminum collecting at 740°C. Here the critical middle layer of electrolyte uses BaF_2 and $BaCl_2$ along with the fluorides of aluminum and sodium for density control.

2.4.2.5 Containment at High Temperatures

The materials available for use as reaction vessels at high temperatures are severely restricted. The erosive effects of mobile melts at and above 700°C upon common refractories have led to a variety of compromise solutions of specific problems. In addition to the destructive diffusion of a melt into the refractory, the frequent tendency of compound formation, the simultaneous action of gases, and electrochemical reactions in specific systems render a general discussion on containment for high temperature electrolytic cells of limited usefulness.

The commercial processes for alkali-metals have most generally become adapted to the use of graphite and steel, including certain stainless steels. For laboratory-type cells, the limited use of quartz is possible.

The use of silver (M.P. 961°C) and a silver chloride cathode is indicated with alkali-metal chlorides. The most refractory oxides (Ca, Y, La, Th) as well as oxides in general suffer from many defects in the proposed use with molten salts and reactive metals such as chemical instability, hydration in air, and structural alteration.

Single-crystal sapphire (Al_2O_3) may be suitable below 900°C. For a given electrochemical system, it will be necessary to evolve the optimum container environment, because latent reactivities to a large number of influences in continuous cyclic processes cannot be predicted from available data. This applies equally to the selection of a stable ceramic separator to be discussed in Section 2.4.4.2 Special composition porcelain has been designed by Labrie and Lamb[70] for the selective conductance of Na^+ in a reversible Ag (AgCl + NaCl) reference electrode, said to be stable and reproducible at 900°C. In this same service, the commercial McDanel shield tubes were also found satisfactory.

2.4.3 Cathode Materials

Available data on the electrochemical behavior of the metal oxide and metal-metal ion electrodes pertinent to the present study is contained mainly in the work of Flengas[57], Delimarskii[48], and Laitinen[71][72] and their co-workers. Presented in Table VIII are data for the electrode potential, theoretical ampere-hour capacity, and reversibility of these materials. In initial studies, to demonstrate the principle of cell construction and type, the silver-silver chloride electrode, although it has a relatively low capacity, is the most desirable cathode material because of the considerable work on it as a reference electrode in molten salts[57]. Other metal-metal ion electrodes in a chloride melt may be more suitable in the design of reversible electrodes supplying power than the metal oxide elec-

trode materials. This would be primarily due to having a mixed molten oxide-chloride electrolyte with the metal oxide electrode.

2.4.4 Methods of Separation

2.4.4.1 Introduction to Separation

The basic problem in the selection of secondary couples using molten salt electrolyte is closely related to the method of separation. The various anode and cathode materials under consideration have been shown to be reversible. In the studies so far, these materials usually show some solubility in the electrolytes. In meeting these problems various methods of separation were evaluated. The most promising method of separation lies in a reaction mechanism which permits single-ion mobility. The principle of this phenomenon is the ability of a single ion to be transported reversibly through either an electrolyte or a ceramic-type material.

2.4.4.2 Ceramics

Certain ceramic materials are commercially available which possess this quality of single-ion mobility[70]. These ceramics are stable, give reproducible results, are temperature-reversible, and, therefore, possess qualities desirable for their suggested application.

At $700^{\circ}C$, a porcelain consisting of Al_2O_3, SiO_2 and Na_2O had a resistivity of 64 ohm-cm. and was able to pass sodium ions reversibly according to Faraday's Law.

A ceramic reference electrode possessing the above characteristics has been developed for use in molten salt systems[70]. This electrode was

permeable to sodium ions and was reversible to these ions. It was used in conjunction with the known reversible electrode AgCl/Ag, thus the entire electrode system behaved reversibly.

In the present study, an evaluation will be made of couples utilizing these materials as separators. These materials should solve the obvious problems encountered in the design of a secondary battery with a molten-salt electrolyte presented by the solubility of the reactant materials.

2.4.4.3 Microporous Separators

The use of a microporous material as a separator in a molten-salt system will also be taken into consideration. A microporous separator, such as a fritted glass disc could be used to separate couples in which the anode and cathode materials have a very low solubility in the melt. The principles involved with this means of separation are:

    a. Selective ion effect and pore size, e.g., ion radius Ba = 1.4

       Li = 0.5

    b. Ion exchange mobility of one ion in a structural material.

More information will be accumulated before any final evaluation of a microporous separator for use in the present application can be made. In particular more data on the solubility of the reactants and products in the melt are required.

2.4.5 Recommended Anode-Cathode Couples for Experimental Evaluation

The electrochemical systems achieving separation by means of single-ion mobility with a ceramic material are the most desirable for the development of a secondary battery with a molten-salt electrolyte.

The selection of anode-cathode couples for experimental evaluation were made on the basis of the criteria of:

    a. Overall system simplicity.

    b. Known reversibility of the components.

    c. Watt-hour capacity of reactant materials.

    d. Ease of handling reactant materials.

    e. Broad representation of reactant materials.

These criteria are listed in the order of relative importance in the selection of anode-cathode couples.

The anode-cathode couples best meeting these criteria are listed in Table IX along with data for the watt-hour per pound capacity of the reactant materials. The estimated operating potentials are determined from the data in Tables VI and VIII, and make the assumption that there is no significant potential drop across the ceramic separator. This assumption is substantiated by the work on reference electrodes utilizing these materials[70][118].

In general, the temperature coefficient of these systems is small as seen by the data for the anodes and cathodes in Tables VI and VIII, respectively.

The experimental cell configurations fall into three basic types:

    a. M_a/Cer./M_aCl, M_cCl/M_c

    b. M_a/M_aCl/Cer./M_aCl, M_cCl/M_c

    c. M_b/M_bCl,NaCl/Cer./NaCl,M_cCl/M_c

where M_a is an anode material whose cation is mobile in the ceramic separator, M_b is an anode material whose cation is not mobile in the ceramic separator, and M_cCl/M_c represents the various metal-metal ion cathode electrodes. The metal-oxide cathodes may be considered as variations of these three basic types in which the metal oxide electrodes function reversibly as electrodes of the second kind. There is experimental evidence to show that the b and c types of cell configurations are reversible[118].

The sodium-silver chloride couple best meets the above criteria and is the best couple to demonstrate feasibility and system simplicity. The cell configuration, type a or b to be used, will be determined by the stability of the separator to metallic sodium. The same will be true for couples with a lithium anode. Data has been presented to show both electrodes are reversible and that the separator is reversible to sodium ions[70]. Specific systems may be represented as follows:

Type a. Na/Cer/NaCl,AgCl/Ag

Type b. Na/NaCl/Cer/NaCl,AgCl/Ag

The KCl-LiCl eutectic may also be used as the electrolyte.

The couples utilizing a magnesium or aluminum anode will use the type c cell configuration. Experimental data are available to show that the Mg-AgCl couple with a ceramic separator is reversible[118]. This couple may be represented as follows:

Mg/MgCl$_2$,NaCl/Cer./NaCl,AgCl/Ag

Other attractive couples with an alkali or alkaline-earth metal anode and metal-metal ion cathode are:

Na/NaCl/Cer/NaCl,CuCl/Cu

Li/LiCl/Cer/LiCl,CuCl/Cu

Mg/MgCl$_2$NaCl/Cer/NaCl,CuCl/Cu

Na/NaCl/Cer/NaCl,NiCl$_2$/Ni
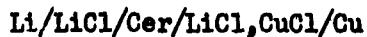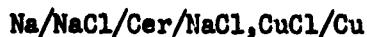
At this time, couples with a metal oxide couple functioning as an electrode of the second kind appear feasible. The couples with a metal oxide cathode that should be considered first are those with a sodium anode and a LiCl-KCl eutectic electrolyte.

The couples to be considered first are:

Na,NaCl/Cer/NaCl,LiCl,KCl,Cu$_2$O/Cu

Na,NaCl/Cer/NaCl,LiCl,KCl,PdO/Pd

Na,NaCl/Cer/NaCl,LiCl,KCl,BiOCl/Bi

After the feasibility of these systems is demonstrated, couples with a magnesium anode will be considered.

Since couples with an aluminum anode demand a fluoride electrolyte, unique separator problems must be solved for cells of the above configuration. For this reason, couples with the aluminum anode should be deferred until the general problems of alkali metal and alkaline-earth metal anodes are evaluated.

2.4.5.1 Experimental Procedure

Experimental_Setup_

Figure 3 illustrates the experimental setup for the initial study of molten salts as electrolytes for use in the present application.

The experimental cell for measurements of e.m.f. and polarization in various anode-cathode couples with a molten electrolyte are shown in Figure 4.

The lower section of this cell, which is used as the container for the molten salt, was constructed of quartz tubing of 40 mm. diameter. This section is connected to a $\overline{S}$50/50 Pyrex ground-glass joint, to permit the interchanging of various electrodes and easy accessibility for the addition of various materials. In this upper section of the cell, there are two joints through which electrical contact is made to the electrodes, a thermocouple well, a gas release valve and a three-way stopcock for gas inlet and a vacuum outlet.

In order to protect the contents of the cell from atmospheric contamination, purified argon gas[36][101] is continually introduced into the cell and excessive gas pressure is released by means of the pressure-release valve.

Some of the precautions that have to be met in this proposed study are:

    a. Good electrical contacts

    b. Preparation (drying) of materials

    c. Contamination hazards

    d. Solubility of metals and salts

    e. Containment

Electrical contacts to the electrodes will vary according to the particular system under evaluation. At present the use of tungsten or

Kovar appears to be most promising for this particular problem. However, other materials such as platinum, silver, gold, and nickel may possibly be used.

The high-melting metals, tantalum ($3000^{\circ}C$) and rhenium ($3440^{\circ}C$), have been employed in salt (Cl^-) melts and in contact with molten metals to some extent, but they involve special problems in shaping. Their stability in molten alkali metals has not been evaluated. Rhenium evolves blinding oxide vapors similar to osmium.

The use of certain stainless steels with the molten active metals is reported, although Fe, Co, Ni, and V, Cr, Mn are severely attacked by liquid Na at moderate temperature.

Any use of these materials which are under consideration will depend upon the severity of thermal and chemical attack on them in a given system. Precautions will be taken to prevent the hydrolysis of the salts that contain water. This may be accomplished in the case of chlorides by the standard method of drying at a high temperature in an HCl atmosphere. This precaution is particularly critical in molten salt studies because any water vapor will permit the formation of H^+ or OH^- ions, which in turn will replace the Cl^- ion in chloride melts.

The formation of an hydroxyl ion in molten salts would lead to corrosive problems at the contact leads and at the electrodes of the system causing electrode polarization in some cases. Other problems due to impurities are listed with the individual anode materials.

The containment problem as discussed in Section 2.4.2.5 will be an important factor in the problem of contamination.

3. CONCLUSIONS

The anode materials are the limiting reactant materials in the selection of new anode-cathode couples for long-life, light-weight secondary batteries in that they determine the solvent system to be used as the electrolyte. Lithium, sodium, magnesium, calcium, and aluminum are the most desirable anode materials on the basis of reactivity and ampere-hour capacity. The available literature shows a molten salt electrolyte, in contrast to other solvent systems, to be the most desirable because:

    a. These anodes are reversible in certain molten salts.

    b. Electrodes may be designed which do not polarise appreciably.

    c. Molten salts have a high electrical conductivity.

A ceramic or porcelain membrane can best meet the requirements of a separator in molten salt electrolyte. Experimental data show that these materials can prevent the mixing of the above reactant materials. A porous separator can be used when the reactant materials have a low solubility in the molten salt electrolyte.

The best cathode materials on the basis of capacity, reversibility and stability in molten salts are:

    a. Metal oxides

    b. Metal-metal ion electrodes

Some of the recommended couples for experimental evaluation are:

    a. Na/NaCl/Cer/AgCl/Ag

    b. Na/NaCl,LiCl/Cer/Cu_2O/Cu

c. Li/LiCl,NaCl/Cer/AgCl/Ag

d. Li/LiCl,NaCl/Cer/CuCl/Cu

e. Mg/MgCl$_2$,NaCl/Cer/AgCl/Ag

f. Mg/MgCl$_2$,NaCl/Cer/CuCl/Cu

g. Na/NaCl/Cer/PdO/Pd

4. RECOMMENDATIONS FOR FUTURE WORK

During the next period effort will be directed to:

a. Evaluate the recommended anode-cathode couples with a ceramic membrane separator.

b. Provide design criteria for the most attractive couples in (a).

c. Consider conditions to provide minimum solubility of reactant materials in order that a porous separator may be used. A porous separator would permit lower operating temperature.

d. Search for other materials that may function as separators with single ion mobility.

Major emphasis will be placed on a and b. Items c and d are logical extensions of the present study.

TABLE I

THEORETICAL PROPERTIES OF SOME POSSIBLE CATHODE MATERIALS*

Cathode Materials	Electrode Reaction	Lbs./500 Amp-Hrs.	Standard Oxidation Potential Ea	Eb
Hydrogen	H(0)-H(I)	0.042	0.00	0.828
Oxygen	O(-II)-O(0)	0.33	-1.23	- .401
m-dinitrobenzene	N(-I)-N(V)	0.59	-0.87[1]	----
Sulfur	S(-II)-S(0)	0.66	-0.141	0.48
Fluorine	F(-I)-F(0)	0.783	-2.87	-2.87
Lithium Bromate	Br(-I)-Br(V)	1.12	-1.44	0.61
Cu$^{++} \rightarrow$ Cu^{o}	Cu(0)-Cu(IIO	1.3	-0.34	----
Osmium Tetroxide	Os(0)-Ps(VIII)	1.3	-0.85	-0.02
Chromium Trioxide and Chromates	Cr(III)-Cr(VI)	1.38	-1.36	0.13
Chlorine	Cl(-I)-Cl(0)	1.46	-1.37	-1.37
Lithium Iodate	I(-I)-I(V)	1.50	-1.08	-0.26
Cuprice Oxide	Cu(0)-Cu(II)	1.65	----	0.224
Manganese Dioxide	Mn(II)-Mn(IV)	1.77	-1.28	----
Nickel Dioxide	Ni(II)-Ni(IV)	1.86	-1.75	-0.49
Rh$^{++} \rightarrow$ Rh^{o}	Rh(0)-Rh(II)	2.10	-0.70	
Pd$^{++} \rightarrow$ Pd^{o}	Pd(0)-Pd(II)	2.20	-0.83	
Nitroquanidine	N(IV)-N(VI)	2.17	-0.88	----
Quinone	2 electron chg.	2.22	-0.70	----
Ag$^{++} \rightarrow$ Ag^{o} (2)	Ag(0)-Ag(I)	2.23	-0.799(2)	-----
Silver Oxide (2)	Ag(0)-Ag(II)	2.54	----	-0.57(2)

TABLE I (Continued)

THEORETICAL PROPERTIES OF SOME POSSIBLE CATHODE MATERIALS*

Cathode Materials	Electrode Reaction	Lbs./500 Amp-Hrs.	Standard Oxidation Potential	
			Ea	Eb
$Au^{+++} \longrightarrow Au^{\circ}$	Au(0)-Au(III)	2.70	-1.42	----
Bromine	Br(-I)-Br(0)	3.30	-1.06	-1.06
Manganese Dioxide	Mn(III)-Mn(IV)	3.50	----	-0.5
Cuprous Chloride	Cu(0)-Cu(I)	3.94	-0.124	----
Mercuric Oxide	Hg(0)-Hg(II)	4.46	----	-0.09
Lead Dioxide	Pb(II)-Pb(IV)	4.85	-1.456	-0.248

* Data from W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd Ed. Prentice-Hall, New York (1952) C. D. Hodgman, Ed., Handbook of Chemistry and Physics, 34th Ed., Chemical Rubber Publishing Co., Cleveland (1952).

(1) E_a for Aniline-Nitrobenzene

(2) Ampere hour capacity for 2 electron change - E_a and E_b for couple indicated.

Anode Material	lbs./500 Amp.Hr.	Electrode Reaction	E_a	E_b
Hydrogen	0.0415	H (0) – H (I)	0.000	0.83
Carbon	0.123	–	–	–
Boron	0.150	–	–	–
Beryllium	0.185	Be (0) – Be (II)	1.70	2.28
Lithium	0.285	Li (0) – Li (I)	3.02	3.02
Aluminum	0.37	Al (0) – Al (III)	1.67	2.35
Titanium	0.49	Ti (0) – Ti (IV)	0.95	
Magnesium	0.50	Mg (0) – Mg (II)	2.34	2.67
Chromium	0.71	Cr (0) – Cr (III)	0.71	1.2
Germanium	0.75	Ge (0) – Ge (IV)	0.15	0.9
Calcium	0.82	Ca (0) – Ca (II)	2.87	3.02
Sodium	0.95	Na (0) – Na (I)	2.71	2.71
Gallium	0.95	Ga (0) – Ga (III)	0.52	1.22
Iron	1.11	Fe (0) – Fe (II)	0.44	0.877
Manganese	1.14	Mn (0) – Mn (II)	1.05	1.47
Zinc	1.34	Zn (0) – Zn (II)	0.76	1.22
Strontium	1.80	Sr (0) – Sr (II)	2.89	2.99
Cerium	1.92	Ce (0) – Ce (III)	2.48	2.75
Rare Earths	>1.92	(0) – III	~2.37	~2.76
Cadmium	2.31	Cd (0) – Cd (II)	0.402	0.815
Lead	4.26	Pb (0) – Pb (II)	0.126	0.578

* Data from W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", 2nd Ed. Prentice-Hall, New York (1952)
C. D. Hodgman, Ed., Handbook of Chemistry and Physics, 34th Ed.;
Chemical Rubber Publishing Co., Cleveland (1952).

TABLE II

THEORETICAL PROPERTIES OF SOME POSSIBLE ANODE MATERIALS*

TABLE III

ELECTRODE POTENTIALS IN VARIOUS SOLVENTS

Electrode	H_2O	CH_3OH	CH_3CN	HCOOH	$HCONH_2$	N_2H_4	NH_3
K/K+	-2.92		-3.02	-2.89	-2.94	-2.93	-2.97
Na/Na+	-2.71	-2.76	-2.73	-2.95		-2.74	-2.84
Li/Li+	-2.96	-3.13	-3.09	-3.01		-3.11	-3.23
Ca/Ca++	-2.76		-2.61	-2.73		-2.82	-2.73
Cu/Cu++	+0.35	+0.31	-0.24	+0.33	+0.21		-0.56
Cu/Cu+	+0.52		-0.14			-0.69	-0.58
Ag/Ag+	+0.80	+0.73	+0.37	+0.64		-0.14	-0.16
Cl/Cl⁻	+1.36	+1.09	+0.72	+1.24			+1.04

TABLE III

ELECTRODE POTENTIALS IN VARIOUS SOLVENTS

Electrode	H_2O	CH_3OH	CH_3CN	$HCOOH$	$HCONH_2$	N_2H_4	NH_3
K/K+	-2.92		-3.02	-2.89	-2.94	-2.93	-2.97
Na/Na+	-2.71	-2.76	-2.73	-2.95		-2.74	-2.84
Li/Li+	-2.96	-3.13	-3.09	-3.01		-3.11	-3.23
Ca/Ca++	-2.76		-2.61	-2.73		-2.82	-2.73
Cu/Cu++	+0.35	+0.31	-0.24	+0.33	+0.21		-0.56
Cu/Cu+	+0.52		-0.14			-0.69	-0.58
Ag/Ag+	+0.80	+0.73	+0.37	+0.64		-0.14	-0.16
Cl/Cl-	+1.36	+1.09	+0.72	+1.24			+1.04

TABLE IV

THEORETICAL CAPACITY OF SOME PROPOSED COUPLES

Couple	Capacity (Watt-Hours) (Per Pound)	Est. Standard Potential (1)
$H_2 - O_2$	1660	1.23
$H_2 - F_2$	1750	2.87
$H_2 - Cl_2$	475	1.37
Be $- O_2$	2620	2.68
Be $- F_2$	2360	4.57
Be $- S$	1100	1.84
Be $- Cu^{++} \rightarrow Cu^0$	765	1.48
Be $- O_8O_4$	860	2.55
Be $- Cl_2$	935	3.07
Be $- MnO_2$	755	2.98
Be $- NiO_2$	845	3.45
Be $- Rh^{+} \rightarrow Rh^0$	525	2.40
Be $- Pd^{++} \rightarrow Pd^0$	530	2.53
Be $-$ Nitroquanidine	550	2.58
Be $-$ Quinone	500	2.40
Mg $- O_2$	1850	3.07
Mg $- S$	980	2.27
Mg $- F_2$	1640	4.21
Mg $- Cu^{++} \rightarrow Cu^0$	740	2.68
Mg $- Cl_2$	945	3.70
Mg $- CuO$	575	2.45
Mg $- MnO_2$	800	3.62
Mg $- NiO_2$	570	3.16
Mg $- Rh^{+} \rightarrow Rh^0$	585	3.04
Mg $-$ Nitroquanidine	590	3.22
Mg $-$ Quinone	560	3.04
Mg $-$ AgO	515	3.14
Cr $- O_2$	770	1.6
Cr $- F_2$	1200	3.58
Cr $- CrO_3$	500	2.07
Mn $- O_2$	595	1.87
Mn $- F_2$	1030	3.92

(1) In couples where there were estimates for both E_A and E_B, the lower estimated standard potential was used.

TABLE IV (Continued)

THEORETICAL CAPACITY OF SOME PROPOSED COUPLES

Couple	Capacity (Watt-Hours) (Per Pound)	Est. Standard Potential
Zn - O_2 (in Acid)	583	1.96
Li - O_2	2760	3.42
Li - S	1350	2.54
Li - F_2	2800	5.90
Li - Cu++→Cu^o	2130	3.36
Li - Cl_2	1250	4.39
Li - CuO	730	2.80
Li - MnO_2	1050	4.30
Li - NiO_2	1120	4.79
Li - Rh+t→Rh^o	780	3.72
Li - Nitroquanidine	800	3.90
Li - Quinone	775	3.72

TABLE V

SOME PHYSICAL PROPERTIES OF CATHODIC COMPOUNDS

	M. P.	B. P.	°C Decomp.
Cupric Oxide	1336		1026
Cuprous Oxide	1235	1800	1800
Antimony Oxide Sb_4O_6	652	1570	
SbOCl	170d	-	170
Ga_2O_3	$\sim$ 450 tr.	1900	-
Ga_2O		Subl. >500	
MnO_2			230+
NiO			400-600($Ni_2O_3 \leftrightarrow NiO$)
PdO	877		877
PtO	555		
Bi_2O_3	(tr. 704) 820-860	1900	
OsO_4	42	135	
Cr_2O_3	1900		
Ag_2O			300
AgO			$\sim$100
Rh_2O_3			1100
HgO			100
$KBrO_3$			370
$K_2Cr_2O_7$			398
KIO_3			560
$KClO_3$			368

Metal	Li	Na	K	Mg	Ca	Al
Amp/Hrs/Lb.	1750	528	474	1000	608	1352
Melting Point °C	186	97.5	62.3	651	810	660
Boiling Point °C	1340	880	760	1110	1200	2057
Metal Chlorides						
Melting Point °C	614	800	770	714	782	192 (SUBL.)
Boiling Point °C	1382	1465	1407	1418	over 1600	178-183 (SUBL.)
Theoretical Std E^0 volts[1] @ 1000°C	3.352	3.019	3.155	2.346	3.208	------
800°C	3.457	3.24	3.441	2.460	3.323	2.097 (180°C)
700°C	3.52	3.34	3.56	2.53	3.38	------
500°C	3.646	3.519	3.755	2.680	3.534	------
Temperature Coefficient of E^0 v/°C	.00059	.0010	.0012	.00067	.0065	------
Electrical Resistance of Chloride K = cm³/ohm	5.8-6.6	2.8-4.0	2.2-3.2	1.1-1.6	2.0	Non Polar
Temperature Range °C	620-800	720-950	780-980	730-1000	800	------

(1) Calculated from thermodynamic data: Reference solvent is pure molten salt.
Reference potential is $(Cl_2, Cl^-) = 0.000$

TABLE VI

PHYSICAL PROPERTIES OF ALKALI AND ALKALINE-EARTH METALS AND ALUMINUM

TABLE VII

SOLUBILITY OF SODIUM IN ITS HALIDES (Ref. 39)

Systems of Na with:

	NaF	NaCl	NaBr	NaI
Consolute Temp. °C	1180	1080	1026	1033
Mole % Na	28	50	52	59
M.P. Pure Salt °C	995	800	747	660
Δ H Calc. Heat of Fusion, Calories	8030	6850	6240	5620
Monotectic Temp. °C	990	7953	740	6567
Mole % Na				
In Salt-Rich Phase (Liquid)	--	2.1	2.9	1.6

Electrode Metal Oxides	Theoretical Capacity Amp-Hours/Lbs.	E.M.F. (volts)	Temperature (°C)	Notes	Ref.
Cu/Cu$_2$O, O$^=$	170	-1.12 to -1.20 [1]	450	Reversible, O = conc. 0.1 M to 0.2 M Electrolyte is LiCl-KCl Eutectic	73
Pt/PtO, O$^=$	115	-0.15 to -0.25 [1]	450	Reversible, O = conc. 0.1 M to 0.2 M Electrolyte is LiCl-KCl Eutectic	73
Pd/PdO, O$^=$	198	-0.34 to -0.45 [1]	450	Reversible, O = conc. 0.1 M to 0.2 M Electrolyte is LiCl-KCl Eutectic	73
Bi/BiOCl, O$^=$	93	-0.78 to -0.90 [1]	450	Reversible, O = conc. 0.1 M to 0.2 M Electrolyte is LiCl-KCl Eutectic	73
Ni/NiO, O$^=$	324	-1.04 to -1.20 [1]	450	Not Reversible, O = conc. 0.1M to 0.2M Electrolyte is LiCl-KCl Eutectic	73
Bi/Bi$_2$O$_3$, O$^=$	52	-0.86 to -0.98 [1]	450	Not Reversible, O = conc. 0.1M to 0.2M Electrolyte is LiCl-KCl Eutectic	73
Pt(II)-Pt(0)		0.000	450	Reference Electrode	
Metal-Metal Ion					
Co(II)-Co(0)	412	-0.991 [2]	450	Reversible, Electrolyte is LiCl-KCl Eutectic	72
Cu(I)-Cu(0)	382	-0.351 [2]	450	Reversible, Electrolyte is LiCl-KCl Eutectic	72
Ga(III)-Ga(0)	523	-0.88 [2]	450	Reversible, Electrolyte is LiCl-KCl Eutectic	72
Ni(II)-Ni(0)	415	-0.795 [2]	450	Reversible, Electrolyte is LiCl-KCl Eutectic	72

TABLE VIII

SOME ELECTROCHEMICAL PROPERTIES OF CATHODE MATERIALS IN MOLTEN SALTS

Electrode Metal Oxides	Theoretical Capacity Amp-Hours/Lbs.	E.M.F. (volts)	Temperature (°C)	Notes	Ref.
Ag(I)–Ag(0)	112	-0.637(2)	450	Reversible, Electro... ... Eutectic	72
Sb(II)–Sb(0)	300	-0.570(2)	450	Reversible, Electrolyte is ...-KCl Eutectic	72
Bi(III)–Bi(0)	174	-0.588(2)	450	Reversible, Electrolyte is LiCl-KCl Eutectic	72
Pd(II)–Pd(0)	227	-0.214(2)	450	Reversible, Electrolyte is LiCl-KCl Eutectic	72
Pt(II)–Pt(0)		0.000	450	Reference Electrode	

Metal-Metal Chloride	Theoretical Capacity Amp-Hours/Lbs.	E.M.F. (volts)	Temp. (°C)	Temp. Coef. volts/°C	Notes
AgCl/Ag	84.5	0.0(3)	700	+0.0014	Reversible, Electrolyte is 1/1 Mole KCl-NaCl
NiCl$_2$/Ni	188	-0.140(3)	700	-0.002	Reversible, Electrolyte is 1/1 Mole KCl-NaCl
CuCl/Cu	122	-0.250(3)	700	+0.0002	Reversible, Electrolyte is 1/1 Mole KCl-NaCl
CoCl$_2$/Co	188	-0.324(3)	700	-0.0002	Reversible, Electrolyte is 1/1 Mole KCl-NaCl

(1) Reference electrode is 1M. Pt
(2) Reference electrode is 1M. Pt: Standard potentials are for unit mole of oxi... ... a mole fraction scale. ... ... is -3.41C ...
(3) Cl$_2$/Cl$^-$ electrode potential at 700°C is +0.31 F on this scale.

TABLE VIII (Continued)

SOME ELECTROCHEMICAL PROPERTIES ... ...

TABLE IX

ESTIMATED WATT-HOUR CAPACITIES OF PROPOSED COUPLES

Anode[2]	Cathode[2]	Est. EMF[1] Volts @ 700°C	Est. Watt-Hours/lb.[2] of Reactant Materials
Li(O)-Li(I)	AgCl/Ag	2.7	230
	CuCl/Cu	2.4	270
	PdO/Pd	3.1	550
	NiCl$_2$/Ni	2.5	420
Na(O)-Na(I)	AgCl/Ag	2.5	190
	CuCl/Cu	2.3	230
	PdO/Pd	2.9	420
	NiCl$_2$Ni	2.4	330
Mg(O)-Mg(II)	AgCl/Ag	1.7	140
	PdO/Pd	2.2	360
	NiCl$_2$Ni	1.6	250

(1) Estimated from EMF data in Tables VI and VIII; Electrode potential Anode material plus electrode potential of cathode material equal estimated cell potential.

Estimated potentials are given to ± 0.1 volt because of slightly different reference states for the various molten salts considered and estimates required for some of the temperature coefficients.

(2) In calculating the cell ampere hour capacities, the ampere hour capacity used for the cathode materials was that chloride or oxide as indicated. This is the more realistic value to use.

References

1. Audrieth, L. F.
   John Wiley & Sons (1953)
   Non-Aqueous Solvents

2. Bertocci, U.
   Zeitschrift Für Elektrochemie 61 (1957) 431
   "The electrochemical behavior of non-aqueous solutions"

3. Brenner, A.
   J. Electrochem Soc. 106 (1959) 148
   "Electrolysis of organic solvents with reference to the electrodeposition
   of metals"

4. Brenner, A.
   J. Electrochem. Soc. 103 (1956) 652-662
   "Electrodeposition of metals from organic solutions"

5. Brenner, A.
   Record of Chemical Progress 16 (1955) 241
   "Electrodeposition of some of the less common metals from non-aqueous media"

6. Brown, O. H., Hsiung, Hsiao-shu
   J. Electrochem. Soc. 107 (1960) 57
   "Polarography in Formamide"

7. Connor, J. H., Reid, W. E., Wood, O. B.
   J. Electrochem. Soc. 104 (1957) 38
   "Electrodeposition of metals from organic solutions", Part V

8. Couch, D. E., Brenner, A.
   J. Electrochem. Soc. 99 (1952) 234
   "A hydride bath for the electrodeposition of aluminum"

9. Dawson, L. R., Warton, W. W.
   J. Electrochem. Soc. 107 (1960) 710
   "Solutions of some alkali halides in the pure liquids and in mixtures of
   N-Methylacetamide and Dimethylacetamide"

10. Dessy, R. E., Handler, O. S.
    J. Am. Chem. Soc. 80 (1958) 5824
    "The constitution of the Grignard Reagent"

11. Fischer, L., Winkler, O., Jander, O.
    Zeitschrift Für Elecktrochemie 62 (1958) 1
    "Recent findings concerning the electrochemistry of non-aqueous solutions"

12. Pultz, E. D., Wood, J. H.
    A.S.T.I.A. Ad 103081 Mcc-1023-TR-73 (1954)
    "Electrolysis studies in organic solvents"

13. Fuoss, R. M., Kirsch, E.
    J. Am. Chem. Soc. 82 (1960) 1013
    "Single ion conductances in non-aqueous solvents"

14. Janz, G. J.
    ARDC Cont. No. AF-18-(600)-33 Proj. Chem. 40-3 Final Report (1956)
    "Standard electrode potentials in non-aqueous solvents"

15. Janz, G. J., Danyluk, S. S.
    J. Am. Chem. Soc. 81 (1959) 3846
    "Hydrogen halides in Acetonitrile"

16. Katzin, L. I.
    J. Inorganic and Nuclear Chemistry 4 (1957) 187
    "Factors affecting the solution of inorganic salts in organic solvents"

17. Kolthoff, I. M., Elving, P. J.
    Interscience Publisher, Inc. (1959)
    Treatise on analytical chemistry, Part I, Section B, No. 9 and 13

18. Koepp, H. M., Wendt, H., Strehlow, H.
    Zeitschrift Für Electrochemie 64 (1960) 483
    "Der Vergleich der spannungsreiken in verschiedenen solventien"

19. Kudra, O. K., Kleibs, G. S.
    Zhurnal Fezecheskoi Khimii 15 (1941) 228
    "The decomposition potentials at various current densities in the systems
    As Br$_3$ - C$_2$ H$_5$ OC$_2$ H$_5$ and SbCl$_3$ - C$_2$ H$_5$ OC$_2$ H$_5$"

20. Lange, J.
    Z. Physikal Chem. 187 (1940) 27
                     186 (1940) 291
    "Electrochemistry of non-aqueous solutions"

21. Mandell, H. C., McNabt, W. M., Hazel, J. F.
    J. Electrochem. Soc. 102 (1955) 263
    "The electrochemistry of some non-aqueous solutions of alkali metal salts"

22. Moeller, T., Cullen, G. W.
    J. Inorg. Nucl. Chem. 10 (1959) 148
    "Observations of the rare earths"

23. Pavlopoulos, T., Strehlow, H.
Zeitschrift für Physicalische Chemie 2 (1954) 90
"Die spannungsreihe in Formamid"

24. Plotnikov, V. A., Yakubson, S. I.
Zhurnal Fezicheskoi Khimii 8 (1936) 159
"An electrochemical investigation of the ternary system $AlBr_3$ - $AsBr_3$ Benzene"

25. Plotnikov, V. A., Yakubson, S. I.
Zhurnal obshchei Khimii 6 (1936) 1694
"An electrochemical investigation of the system $AlBr_2$ - $AsBr_3$ in ethyl bromide"

26. Plotnikov, V. A.
Mem. Inst. Chem. Ukrain, Acad. Sci. 5 (1938) 271
"Non-aqueous solutions"

27. Reid, W. E., Jr., Bish, J. M., Brenner, A.
J. Electrochem. Soc. 104 (1957) 21
"Electrodeposition of metals from organic solutions" Part III

28. Schaschl, E.
J. Electrochem. Soc. 94 (1948) 299
"Non-aqueous battery systems"

29. Strehlow, H.
Zeitschrift für Elektrochemie 56 (1952) 827
"Der vergleich der spannungsreihen in verschieden solventien"

30. Strehlow, H., Koepp, H. M.
Zeitschrift für Elektrochemie 62 (1958) 373
"Uber auswahlende Solvation von Ionen in Losungsmittelgemischen"

31. Ussanowitch, U.
Acta Physiochimica USSR 2 (1935) 239
"The nature of the conductivity of non-aqueous solutions"

32. Ussanowitch, U.
Zeitschrift für physikalische Chemie 124 (1926) 427
"The electrical conductivity of the system: Arsenic Tribromide - ethyl ether"

33. Vedel, J., Tremillon, B.
J. Electroanal. Chem. 1 (1959-60) 241
"Voltammetui Du Systeme Hydrogene - Acide Perchlorique Dams L' Acetonitrile, A Une Electrode De Platine Platine"

34. Antipin, L. N., Kholanaskikh, Y. B.
    Zhur Fiz Chim $\underline{31}$ (1957) 232
    "Electric potential in fused salts"

35. Aziz, P. M. Wetmore, F. W.
    Can. J. Chem. $\underline{30}$ (1952) 779
    "Molten salts - Electrical transport in the system $AgNO_3$ - $NaNO_3$"

36. Bockris, J. O'M., White, J. L., Mackensie, J. D.
    Academic Press Inc. (1959)
    Physico - chemical measurements at high temperatures

37. Bockris, J. O'M.
    Trans. Faraday Soc. (1959) 1904
    "Reversible system U/U Cl_3, Li Cl + K Cl/KCl + Li Cl, Ag Cl/Ag"

38. Bockris, J. O'M.
    J. Sci. Instrum. $\underline{33}$ (1956) 438
    "An all-glass reference electrode for molten salt systems"

39. Bredig, M. A., et al
    J. Am. Chem. Soc. $\underline{77}$ (1955) 307
    Misability of liquid metals with salts

40. Broers, G. H. J., Ketelaar, J. A. A.
    Abst. from Thesis by G. H. J. Broers (1958)
    "High temperature fuel cells"

41. Byrne, J., Fleming, H.
    Can. J. Chem. $\underline{30}$ (1952) 922
    "Electrical conductivity in the system $AgNO_3$ - $NaNO_3$"

42. Chambers, H. M., Taptram, A. D. S.
    Am. Chem. Soc., Div. of Gas and Fuel Chemistry, Atlantic City, N. J.
    (1958)
    "Carbonaceous Fuel Cells"

43. Cowen, H. C., Axon, H. J.
    Trans. Faraday, Soc. $\underline{52}$ (1956) 242
    "The electrical conductivity of the binary fused salt systems $AgNO_3$ + KNO_3
    and $AgNO_3$ + $LiNO_3$"

44. Delimarskii, Yu. K.
    Zhur Prikl Khumii $\underline{30}$ (1957) 406-411
    "The dissociation potentials of the fused LiCl-K Cl and Li Cl - Ba Cl_2
    systems"

45. Delimarskii, Yu. K.
    Ukrain Khim Zhur 16 (1950) 414
    "Electrochemical series of metals in fused salts"

46. Delimarkii, Yu. K.
    Ukrain Khim Zhur 15 (1949) 340-50
    "Determination of electrode potentials of metals in molten bromides with
        the aid of glass - sodium electrode"

47. Delimarskii, Yu. K., Grigorenko, F. F.
    Ukrain Khim Zhur 22 (1956) 726-30
    "Polarization EMF on electrolysis of melted flourides"

48. Delimarskii, Yu, K.
    Zhur Fiz Khim 29 (1955) 28-38
    "The electrode potentials of metals in molten salts"

49. Didlschenko, R., Rochow, E. C.
    J. Am. Chem. Soc. 76 (1954) 3291
    "Electrical potentials in molten silicates"

50. Duke, F. R.
    J. Electrochem. Soc. 105 (1958) 476
    "Mobilities of the ions in fused KNO_3 - $AgNO_3$ mixtures"

51. Duke, F. R.
    J. Electrochem. Soc. 105 (1958) 548
    "Transport numbers of the pure fused salts $LiNO_3$, $NaNO_3$, KNO_3, and $AgNO_3$"

52. Duke, F. R.
    J. Electrochem. Soc. 106 (1959) 130
    "Transport numbers and ionic mobilities in the system KCl - $PbCl_2$"

53. Duke, F. R.
    J. Electrochem. Soc. 104 (1957) 251
    "Density and conductance in the system $K Cl$ - $Zn Cl_2$"

54. Duke, F. R.
    J. Phys. Chem. 59 (1955) 549
    "The measurement of transport numbers in pure fused salts"

55. Dworkin, A. S.
    J. Phys. Chem. 64 (1960) 269
    "The heat of fusion of the alkali metal halides"

56. Eisen, O. A.
    Zhur Fiz Khim 30 (1956) 3
    "Electrochemistry of Molten Oxides"

57. Flengas, S. N., Ingraham, T. R.
    Can. J. Chem. 35 (1957) 1254
    "Voltaic cells in fused salts"

58. Grjotheim, K.
    Z. Physik, Chem. (Frank) II, (1957) 150
    "Electrochemical series of metals in the eutectic melt of sodium-potassium-fluorides"

59. Grimes, W. R.
    J. Phys. Chem. 62 (1958) 862
    "Solubility of Noble gases in molten fluorides"

60. Grimes, W. R.
    J. Phys. Chem. 621 (1958) 1325
    "Thermodynamic properties of molten and solid solutions of Ag Cl and Na Cl"

61. Gurovich, E. I. Matveiva, M. S.
    Zhur Fis Khim 33 (1959) 2607
    "Measurement of the potentials for metals in fused salts"

62. Hamer, W. J., Schrodt, J. P.
    J. Am. Chem. Soc. 71 (1949) 2347
    "Galvanic cells with solid and molten electrolytes"

63. Hamer, W. J., Malmborg, M. S., and Rubing, B.
    J. Electrochem. Soc. 103 (1956) 8
    "Theoretical electromotive force for cells containing solid or molten chloride electrolytes"

64. Hill, D. L.
    J. Electrochem. Soc. 107 (1960) 698
    "An electrochemical study of uranium in fused chlorides"

65. Hill, Derek L., Osteryoung, Robert
    U. S. At. Energy Comm. BNL - 588 (T-166)
    "Chemical behavior of uranium and thorium in fused salts"

66. Hvorka, Frank
    J. Electrochem. Soc. 106 (1959) 56
    "The oxygen electrode"

67. Inman, D., Hills, G. L., Bockris, J. O'M.
    Trans. Faraday Soc. 55 (1959) 1904
    "Electrode reactions in molten salts"

68. Janz, G. L., Solomons, C., Gardner, H. J.
    Chem. Reviews 58 (1958) 461
    "Physical properties and constitution of molten salts"

69. Kingerly, W. D.
Proc. Sym. of High temperature (1956)
"Corrosion of refractories by oxides"

70. Labrie, R. J., Lamb, V. A.
J. Electrochem. Soc. 106 (1959) 895
"A porcelain reference electrode"

71. Laitinen, H. A., Liu, C. H.
J. Am. Chem. Soc. 80 (1958) 1015
"E.M.F. Series in molten Li Cl - KCl eutectic"

72. Laitinen, H. A., Bhatia, B. B.
J. Electrochem. Soc. 107 (1960) 705
"E.M.F. study of metallic oxides in fused Li Cl - KCl eutectic"

73. Laity, R. W.
J. Electrochem. Soc. 105 (1958) 97
"Transport numbers in pure fused salts"

74. Laity, R. W.
J. Electrochem. Soc. 104 (1957) 299
"Transport numbers and structures in fused Ag NO_3 - Na NO_3 mixtures"

75. Livey, D. T.
J. Less, Common Metals 1 (1959) 145
"High temperature stability of oxides and sulfides"

76. Lunden, A.
Contract W-7405 Eng. 82 (Apr. '60)
"Transport numbers in pure fused Zn Cl_2

77. Lunden, A.
Am. N. Y. Acad. Sci. 79 (1960) Art. 11, 988-96
"Fused salt isotope enrichment by electromigration"

78. Lundon, G. J., Ubbelohde, A. R.
Proc. Roy. Soc. 240 (1957) 160
"Melting and crystal structure of Cryolite (3NaF, Al F_3)"

79. Mantell, C. L.
McGraw-Hill Publishers (1960)
Industrial electrochemistry 4th edition

80. Martin, R. L.
J. Chem. Soc. 157 (1954) 3246
"Activation energy of electrical conductivity in fused electrolytes"

81. Markov, B. F.
     Doklady Acad. Nauk. SSSR 108 (1956) 115
     "Electromotive force at high temperatures in molten salts"

82. Markov, B. F., Delimarskii, Yu. K.
     Zhur Fiz Khim 29 (1955) 51
     "Thermodynamic properties of Mg Cl_2 in the melt Mg Cl_2 - Li Cl, Mg Cl_2 -
     Na Cl, Mg Cl_2 - K Cl, Mg Cl_2 - Rb Cl"

83. Markov, B. F.
     . kad. Nauk Ukr. SSR (1959) No. 2, 216-30
     "E.M.F. of chemical cells with a single fused salt"

84. Maskovets, V. P., Revazyan, A. A.
     Zhur Priklad Khim 30 (1952) 1006
     "E.M.F. of galvanic cells of fused cyrolite - alumina"

85. McGraw-Hill Publishers (1955)
     Reactor Handbook 1st Edition

86. McGraw-Hill Publishers (1960)
     Proceedings of an International Symposium on High Temperature
     Technology

87. Milazzo, Giulio
     J. Electroanal. Chem. 1 (1960) 265-84
     "Reference electrodes and potentials"

88. Minenko, V. I., Pitrov, S. M.
     Ukrain Khim Zhur 26 (1960) 195
     "E.M.F. Study of the PbO - SiO_2 system"

89. Morachevskii, A. G.
     Zhur Priklad Khim 33 (1960) 1434
     "Review of studies in the field of electrochemistry of fused salts for 1959"

90. Peterson, A., Gregor, Harry
     J. Electrochem. 106 (1959) 1051
     "Diffusion exchange of exchange ions and nonexchange electrolyte in ion-
     exchange membrane system"

91. Piontelli, R.
     Annals of N.Y. Acad. of Sci. 79 (1960) 1025
     "Reference electrodes and overvoltage measurements in molten salts"

92. Piontelli, R., Montanelli, G.
     J. Chem. Phys. 23 (1954) 1781
     "Cell for measurements of polarization voltages in melted electrolytes"

93. Piontelli, R., Sternheim, G.
    J. Chem. Phys. 23 (1955) 1358, 1971
    "Overvoltages in melted electrolytes"

94. Protsenko, P. I., Shokenia, O. N.
    Russian J. of Inorganic Chem. (1960) 437, 208
    "Electrical conductivity in the ternary system of the nitrites of Na,
    K, Ba"

95. Roake, W. E.
    J. Electrochem. Soc. 104 (1957) 661
    "The systems CaF_2 - LiF and CaF_2 - LiF - MgF_2"

96. Rogers, S. E., Ubbelohde, A. R.
    Trans. Far. Soc. 46 (1950) 1051
    "Acid sulfates low melting"

97. Rosenberg, N. W.
    J. Electrochem. Soc. 104 (1957) 111
    "Electrochemical properties of a cation - transfer membrane"

98. Selis, S. M., McGinnis, L. P.
    J. Electrochem. Soc. 106 (1959) 134
    "Galvanic behavior in fused electrolytes"
    I. The nominal system Mg/LiCl - KCl/Ni

99. Selis, S. M., McGinnis, L. P.
    J. Electrochem. Soc. 106 (1959) 990
    "Galvanic behavior in fused electrolytes"
    II. Discharge of the system Mg/LiCl - KCl - K_2CrO_4/Ni

100. Senderoff, S., Mellors, G. W.
     Rev. Sci. Inst. 29 (1958) 151
     "Reversible chlorine electrode for the measurement of E.M.F. in molten
     salt cells"

101. Seybolt, A. V., Burke, J. E.
     John Wiley and Sons, Inc. (1953)
     Procedures in experimental metallurgy

102. Sidgwick, N. V.
     Oxford Press (1950)
     The chemical elements and their compounds, Vol. I and II

103. Smithells, C. J.
     Interscience Publishers
     Metals reference handbook (2 vols.)

104. Spiegler, K. S.
    J. Electrochem. Soc. 100 (1953) 303C
    "On the electrochemistry of ion-exchange resins"

105. Stern, K. H.
    J. Phys. Chem. 60 (1956) 1443
    "Electrode potentials in fused systems"

106. Stern, M., Wissenberg, H.
    J. Electrochem. Soc. 106 (1959) 755
    "Electrochemical behavior and passivity of Titanium"

107. Straumanis, M. E., Schlechten, A. W.
    J. Electrochem. Soc. 102 (1955) 131
    "Electrochemical behavior of a Titanium - fused salt platinium cell"

108. Sundheim, B. R.
    J. Phys. Chem. 60 (1956) 1381
    "Transference numbers in molten salts"

109. Suskii, L.
    Zhur Fiz Khim 30 (1956) 1855-9
    "E.M.F. of the cells Pb/PbCl$_2$/Cl$_2$ and Po/PbCl$_2$/Na Cl 50 mole per cent
       Cl$_2$ in fused state"

110. Tipton, C. R., Jr.
    Interscience Publishers (1960)
    Reactor handbook, 2nd Edition

111. Trzebiatowski, W., Kisza, A.
    Bull Acad. Polon Sci., 7 (1959) 781-7
    "Electrode potentials of Uranium in molten salts"

112. Van Arkel, A. E., Flood, A. E.
    Can. J. Chem. 31 (1953) 100
    "Conductivity of molten oxide"

113. Van Artsdalen, E. R.
    J. Phy. Chem. 59 (1955) 118
    "Electrical conductance and density of molten salt systems: KCl - Li Cl,
       KCl - Na Cl and KCl - KI"

114. Valsbavek, E., Belyaev, A. J.
    Sbornik Nauch. Trudcv. Moskov, Inst. Tevetnoi Metal i Zolota (1957)
       No. 27 163-77
    "Study of melts of a Cryolite - Alumina - Aluminum Fluoride Magnesium
       Fluoride System as electrolyte for the Aluminum bath".

115. Verdieck, R. G., Yutema, L. F.
     J. Phys. Chem. 46 (1942) 344
     "Electrochemistry of fused aluminum halides"

116. Wagner, Carl
     J. Electrochem. Soc. 104 (1957) 308
     "Galvanic cells for the determination of the standard molar free energy
        of formation of metal halides, oxides and sulfides at elevated
        temperatures"

117. Welde, A. F.
     Dissertation Abst. 20 (1959) 1199
     "Electrochemical study of fused salts"

118. Yang, Ling, Hudson, R. G.
     J. Electrochem. Soc. 106 (1959) 986
     "Some investigations of the Ag/Ag Cl in LiCl-KCl eutectic reference
        electrode"

119. Yim, E. W., Fleinleib, M. J.
     J. Electrochem. Soc. 104 (1957) 626
     "Electrical conductivity of molten fluorides"

120. Yim, Ernest, Feinlieb, Morris
     J. Electrochem. Soc. 104 (1957) 622, 630
     "Electrical conductivity of molten fluorides"

121. Zaretskii, S. A., Machvkas, V. B.
     Zhur Vaesoyuz 5 (1960) 357
     "New methods of potassium production"

122. Zoseniovich, D. P., Tsemnergahl, V. A.
     Ukrain Khim Zhur 15 (1949) 351-61
     "Decomposition potentials of metal oxides in molten Na OH"

APPENDIX A - ILLUSTRATIONS
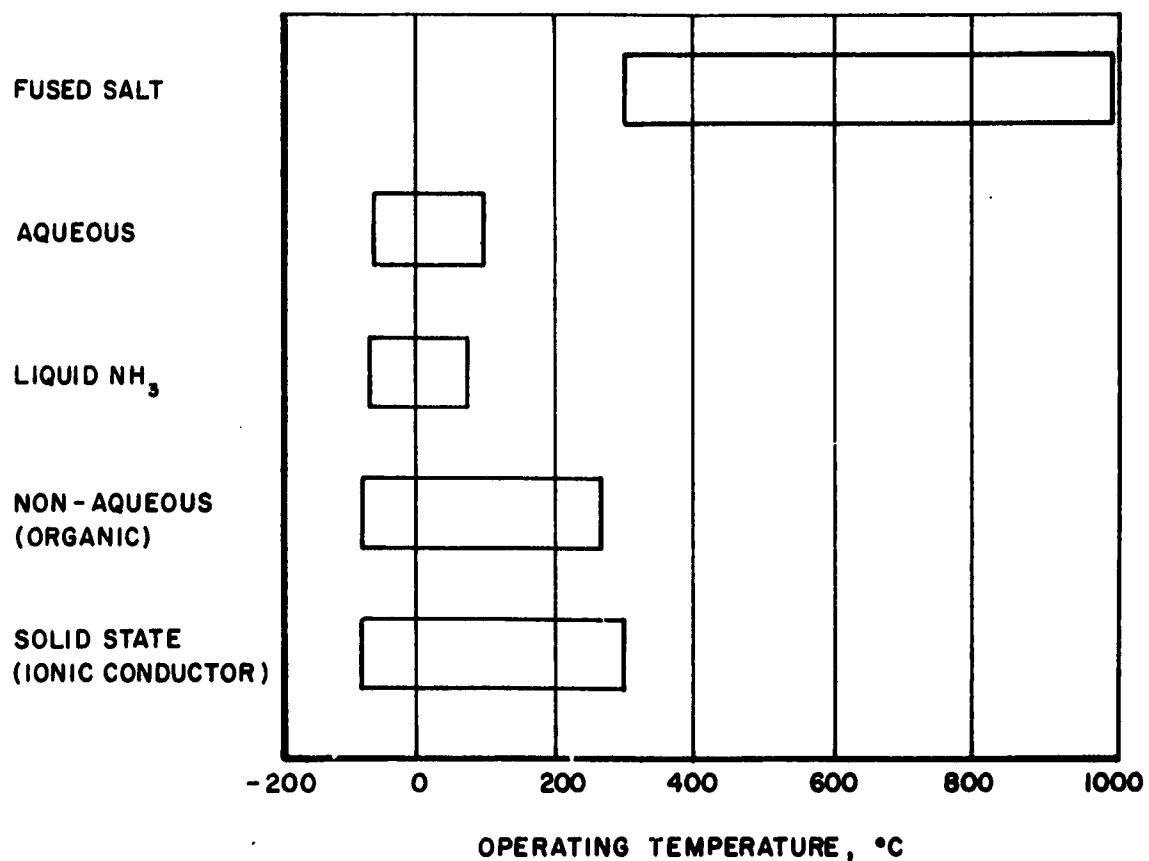
Fig.1   Typical Temperature Ranges For Various Electrolytes
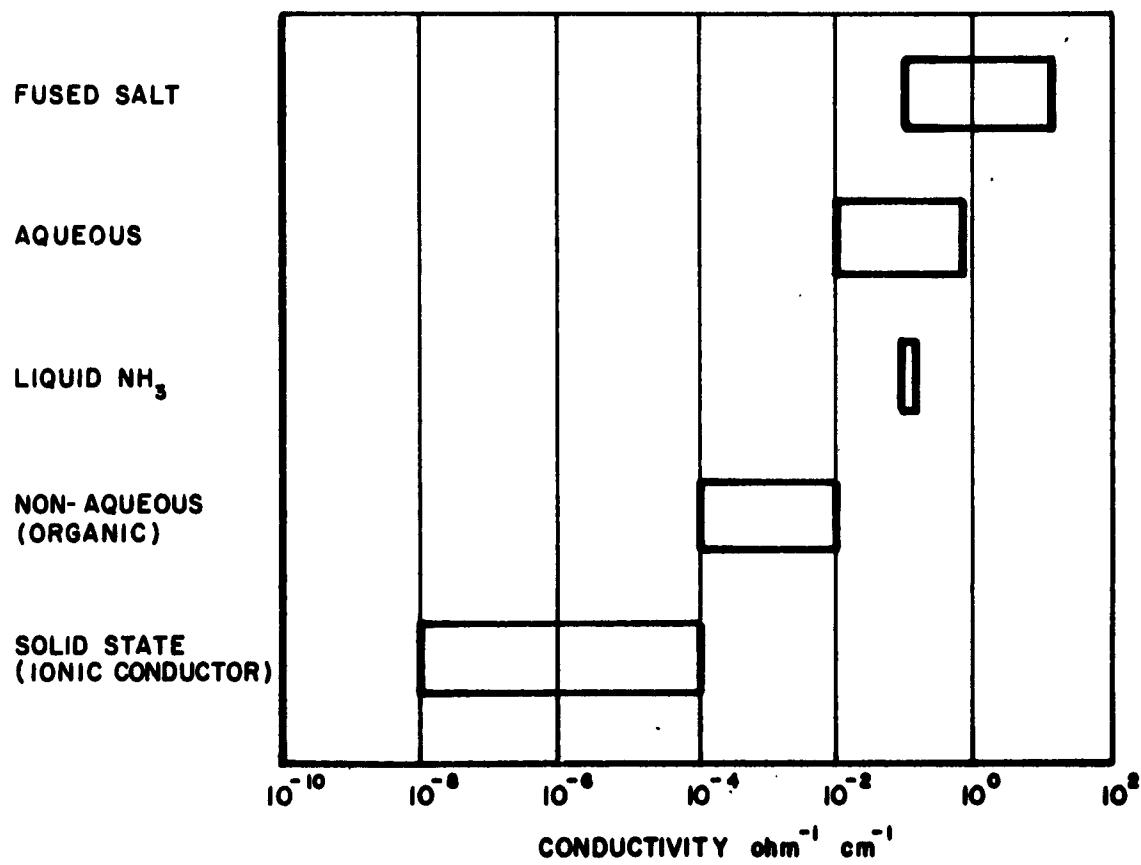
Fig. 2 Typical Conductivity Ranges For Various Electrolytes
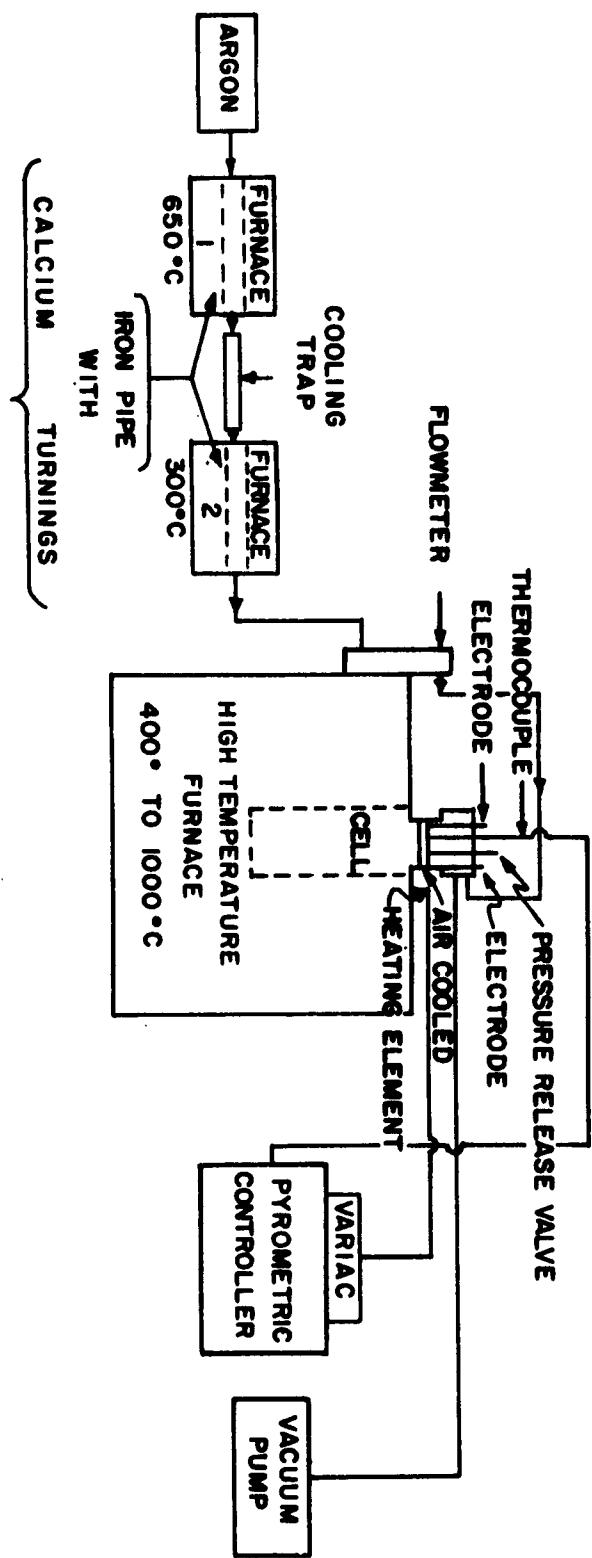
Fig. 3 Experimental Setup For Molten Salt Study
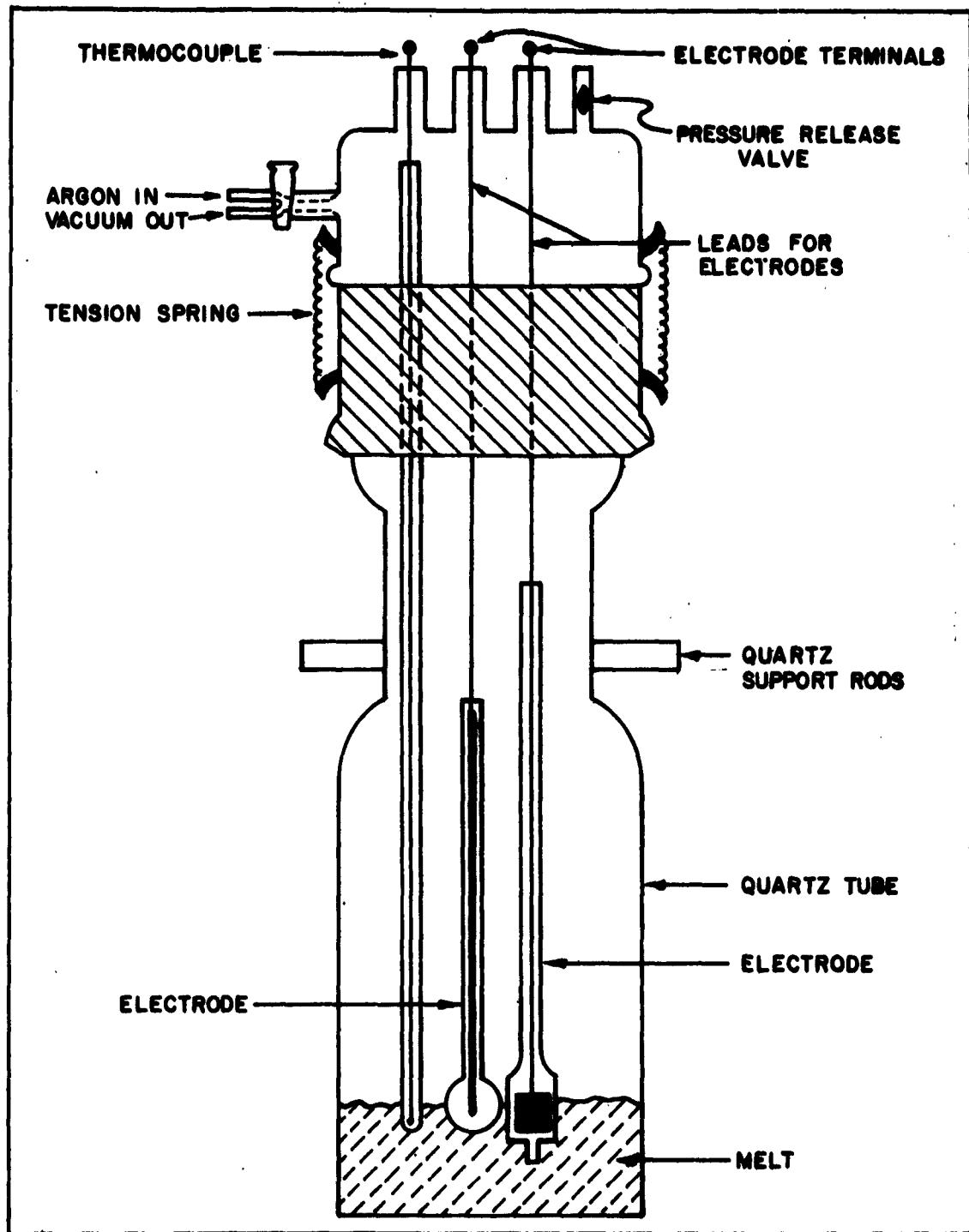
Fig. 4 Experimental Cell For Molten Salt Study